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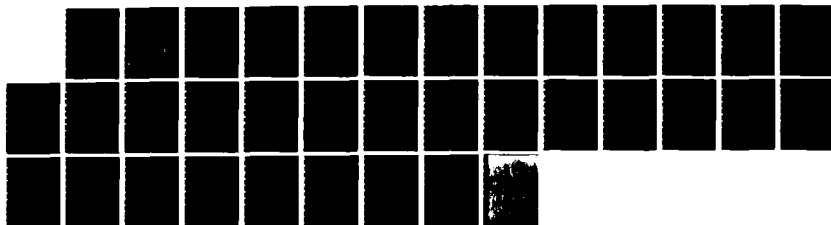
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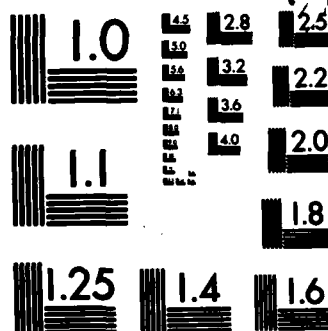
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Edwin R. Alvarez-Roa, Nelson E. Prieto and Charles R. Martin

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Luminescence Titrations of Polyelectrolytes

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(AC830786X)

Brief

The equivalent weight (g polymer per mole of charged sites) of a hydrophobic polyanion or the concentration of such a polyanion in solution can be determined by a new luminescence titration procedure using a hydrophobic cationic lumophore.

Abstract

When an anionic polyelectrolyte is added to a solution of a cationic lumophore (the probe), binding of the probe ions to the anionic sites on the polymer chain can occur. We have found that in some cases, this binding results in an increase in the probe's quantum yield for emission. This paper explores the possibility of exploiting this effect in luminescence titrations for determination of either the equivalent weight (EW) of a polyanion or the concentration of the polyanion in solution (if the EW is known). A suitable probe cation is identified and luminescence titration curves for a variety of polyanions are presented. The luminescence titration procedure was found to produce precisions of better than 5% and accuracies of better than 1% in titrations of the Na^+ salt forms of hydrophobic polyanions.

Introduction

Because polyelectrolytes are used extensively in wastewater treatment procedures (1,2), reliable means for determination of polyelectrolyte concentrations in wastewater solutions are required (2). Polyelectrolytes are also seeing increasing use as agents for the preparation of chemically modified electrodes (3,4). The equivalent weight (EW) of the polyelectrolyte (i.e., grams polymer per mole of charged sites) is of primal importance for these applications since the EW will determine how many moles of electroactive counterions can be attached to a modified electrode surface. Accurate procedures for determination of EWs of polyelectrolytes are, therefore, also required. For example, we have recently reported a procedure for dissolving DuPont's Nafion polymers (5); because this procedure uses elevated temperatures and pressures it was important to assess whether any damage occurred to the polyion during the dissolution procedure (5). One way of assessing this is through an EW determination (5). McGrath, et al. (6) have also recently pointed out the importance of equivalent weight determinations of ion-containing polymers and have commented on some of the difficulties in current methodologies.

The luminescence probe technique has proved to be useful for studying the chemical and morphological characteristics of polyelectrolytes (7-18). We recently reported (16) a luminescence probe study of the polyelectrolytes obtained by dissolving (5) the Nafion polymers. During these studies, we discovered that when a solution of Nafion is added to a solution of the lumophore $\text{Ru}(\text{bpy})_3^{2+}$ (bpy = 2,2'-bipyridine), $\text{Ru}(\text{bpy})_3^{2+}$ emission intensity increased until a roughly, stoichiometrically equivalent amount of the Nafion was added, after which a leveling in emission intensity occurred (16). Similar results were recently reported by Kurimura, et al. in a luminescence

probe study of a sulfonated polystyrene (15) and by Nagata and Okamoto using Tb^{3+} and various polyelectrolytes (18).

Because the emission intensity for $Ru(bpy)_3^{2+}$ leveled after the addition of stoichiometrically equivalent amounts of these polyions, it seemed that this effect could be exploited in a luminescence titration procedure for either a determination of the EW of a polyelectrolyte or a determination of the concentration (g per unit volume) of a polyelectrolyte solution, if the EW is known. We have conducted a series of experiments aimed at testing the viability of this proposed titration procedure. Specifically, we have attempted to identify suitable luminescent probe cations for the proposed titrations and to identify the types of polyelectrolytes which can be successfully titrated using this procedure. We have also evaluated the accuracy and precision of the luminescence titration procedure for selected test polyelectrolytes. Results of these, and related, studies are described here.

EXPERIMENTAL SECTION

Materials. $Ru(bpy)_3(Cl)_2$ (G. F. Smith) and [1-dimethylaminonaphthalene-5-sulfonamidoethyl]trimethylammonium perchlorate (the cation is abbreviated DA^+ ; obtained from Sigma) were used as received. Fresh solutions of DA^+ were prepared daily. 1100 equivalent weight Nafion was donated by E. I. DuPont de Nemours; Nafion solutions were prepared using the procedure of Martin, et al. (5). Sodium poly(styrene sulfonate), 100% sulfonated (100-NaPSS), sodium poly(styrene sulfonate), 50% sulfonated (50-NaPSS), poly(methacrylic acid-methylmethacrylate), 20% carboxylated (PMM), and sodium poly(anethole sulfonate), 100% sulfonated (NaPAS) were obtained from Polysciences. Sodium poly(styrene sulfonate), 6% sulfonated (6-NaPSS) was a gift from R. D. Lundberg of Exxon Research and Engineering Company.

MilliQ (millipore Water Systems) and triply distilled water were used. All other reagents and solvents were of the highest grade obtainable.

Polymer Purification. PMM and 6-NaPSS were used as received and dissolved in dimethylsulfoxide. The Nafion solution (5) was dialyzed against 50:50 ethanol-H₂O for three days; the ethanol-H₂O on the outside of the dialysis tube was changed every six hours. After dialysis, the concentration of the solution was determined by evaporating a volume to dryness and weighing the residue. All other polymers were dissolved in water and recrystallized from acetone. Aqueous stock solutions (0.1 to 0.5 w/v%) were prepared from the recrystallized materials. While these solutions should be quite stable, fresh solutions were prepared before each study.

Luminescence Titration Procedure. Luminescence titrations were performed by adding a known volume of a solution of the lumophore (either Ru(bpy)₃²⁺ or DA⁺) to a quartz cuvette, obtaining the initial luminescence spectrum, and then adding increments of the stock polymer solution to the cuvette, obtaining spectra after each addition. The cuvette solution was thoroughly mixed after each addition. The Na⁺ forms of all of the polyanions were used, except in studies aimed at determining the effect of H₃O⁺, where the proton forms were used. The Na⁺ forms of Nafion and PMM were prepared, immediately before use, by adding carefully measured volumes of an NaOH solution to the polymer solutions. In cases where a non-aqueous solvent was used to dissolve the polymer (Nafion, 6-NaPSS and PMM) increments of the solvent, without polymer, were added to lumophore solutions and luminescence spectra obtained. These blank titrations were run to be sure that the small (generally less than about 50 μ L) amounts of organic solvent added did not affect the luminescence of the fluorophore.

No effects were observed.

A Spex Fluorolog 2 spectrofluorometer was used; $\text{Ru}(\text{bpy})_3^{2+}$ and DA^+ were excited at 450 and 336 nm, respectively. Quantum yields were determined using a modified Parker and Rees method (19).

Acid-Base Titrations. The proton forms of 100-NaPSS and 50-NaPSS were prepared via ion exchange using a column of Bio-Rad's analytical grade macroporous cation exchange resin (AG MP-50). The concentrations of the polymer solutions were determined, after conversion to the H^+ form, by evaporating and weighing. Aqueous solutions of the H^+ form polymers were titrated with NaOH using phenol red as the indicator.

RESULTS AND DISCUSSION

Theoretical Considerations. When a solution of a polyanion is added to a solution of a probe cation, a probe cation may bind to an anionic site on the polymer chain, producing a so-called complex (18); these reactions may be described by



where L^+ is the luminescent probe, $\text{S}^- - \text{Na}^+$ is an anionic site on the polyion (which initially has Na^+ as its counterion), and C is a complex. For simplicity, 1:1 stoichiometry is assumed in equation 1. The extent of this reaction is determined by the magnitude of the equilibrium constant, K (14,18,20-26).

$$K = \frac{[\text{C}]^2}{[\text{L}^+][\text{S}^- - \text{Na}^+]} \quad (2)$$

The basis of the titration procedure proposed here is that the quantum yield for the complexed lumophore (ϕ_c) is greater than that for the free lumophore (ϕ_L) (10,11). Therefore, as polyion is added to the lumophore solution, an increase in emission intensity is observed. Typical emission spectra for the cationic probes DA^+ and $Ru(bpy)_3^{2+}$, which demonstrate this effect, are shown in Figure 1.

Because the concentration of lumophore is low, the emission intensity before the addition of any polyion (I_0) is given by (27)

$$I_0 = A\phi_L[L]_0 \quad (3)$$

where A is a constant and $[L]_0$ is the initial concentration of the lumophore. Because the absorptivities of the lumophores used here do not change upon binding to the polyion (16), the emission intensity after the addition of an increment of polyion solution (I) is given by (27).

$$I = A\phi_L[L] + A\phi_c[C] \quad (4)$$

When sufficient polyion is added, essentially all of the lumophore will become complexed and I will reach a maximum value (I_{max}) (23), given by

$$I_{max} = A\phi_c[L]_0 \quad (5)$$

(Equation 5 assumes that such small volumes of polyion solution are added that there is no dilution.) Mathematical modeling (Figure 2) shows that if K and the concentration of polyelectrolyte are sufficiently large, I_{max} will be reached after a small excess of polyelectrolyte solution has been added. Standard (28) extrapolation procedures may then be used to identify the equivalence point volume (Figure 2).

If the concentration of the polymer solution (C_p) is known, the equivalence point volume (V_E) can be used to calculate the EW of the polyanion.

$$EW(\text{g/mole}) = V_E(\text{mL}) \times C_p(\text{g/mL}) \times 1/\text{moles probe} \quad (6)$$

Alternatively, if the EW is known, C_p may be calculated.

$$C_p(\text{g/mL}) = \frac{\text{moles probe}}{V_E(\text{mL})} \times EW(\text{g/mole}) \quad (7)$$

Units in equations 6 and 7 are given in parenthesis and 1:1 stoichiometry between the probe and site is assumed.

Evaluation of the Titration Procedure. The mathematical simulations (Figure 2) indicate that, as is the case in any titration procedure, location of the endpoint volume is easiest when sharply breaking titration curves are obtained. Figure 3 shows that the probe used in our previous study (16), $\text{Ru}(\text{bpy})_3^{2+}$, produces gradually breaking curves for all of the polyelectrolytes studied here; $\text{Ru}(\text{bpy})_3^{2+}$ is not the optimal probe. Titration curves for the cationic probe DA^+ are shown in Figure 4. These curves have much sharper breaks. Subsequent studies of the accuracy and precision of the titration procedure used DA^+ as the probe cation.

The precision of the luminescence titration procedure was evaluated by running three or four replicate titrations of polyelectrolyte solutions of known concentration and calculating average EWs and standard deviations for these average EWs. The Na^+ forms (vide infra) of the polyelectrolytes were used. Relative standard deviations of better than 5% were obtained (Table I). Accuracy was evaluated by comparing results (average EWs) obtained from the luminescence procedure with results obtained from a standard method (acid-base titration). The two methods produced identical

results (Table I). Furthermore, the results of both methods agreed, within experimental error, with the nominal EW values specified by the supplier.

As indicated by the mathematical simulations (Figure 2), strong polyion-counterion interactions (i.e., large K 's) are required if sharply breaking titration curves are to be obtained. It has been well documented that the strength of the polyion-counterion interaction is enhanced when hydrophobic (as well as electrostatic) interactions are possible (14-16). Because hydrophobic probes are used, the luminescence titration procedure described here would be expected to have greater applicability to hydrophobic polyanions. The data shown in Figures 3 and 4 support this conclusion in that sharper titration curve breaks are observed for the polyions containing hydrophobic groups (i.e., CF_2 or phenyl rings). This conclusion is also supported by Meisel and Matheson who found that polyvinylsulfate (a hydrophilic polyanion) has no effect on the emission spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ (29).

For the titration procedures described here to be practical, there must be minimal interference from monomeric ions. The most common and potentially most significant source of such interference is what we will call mass action interference. Mass action interference results from the effect of Na^+ (or other cation) on the position of equilibrium in equation 1. In the presence of added salt, the position of equilibrium should shift to the left causing more curvature in the luminescence titration curve (Figure 5). The severity of this type of interference will depend on the magnitude of the probe-polyion binding constant. Because the binding constants for Nafion and the styrene-based polyions are so large, huge excesses of salt can be tolerated (16). For example, Figure 5 shows the curve for the titration of $2.3 \times 10^{-5} \text{ M DA}^+$ with 100-NaPSS, in the

presence of 10^{-2} M NaCl. Despite the greater than 400-fold excess of Na^+ , the equivalence point volume can still be easily determined. Species which quench the excited state of the probe may also act as interferants. We are currently identifying species which strongly quench DA^{++} so that the severity of this potential source of interference can be evaluated.

In any analytical procedure, it is important to know the lowest level of analyte which can be reliably determined. Unfortunately, as is the case with many analytical methods (30), the lowest polyion concentration which can be reliably titrated using this procedure will depend on, among other factors, whether interferants are present. In the simplest case (no interferants), the detection limit is, in principle, determined by the magnitude of the probe-polyion binding constant. In practice, however, lower polyion concentrations will necessitate using lower probe solution concentrations. The detection limit for this method is, therefore, ultimately limited by the quantum yield of the probe and the magnitude of the change in the quantum yield upon binding. With the current probe, DA^+ , we have successfully titrated Nafion solutions with concentrations as low as 0.047%.

The Effect of H_3O^+ . The data presented to date show that the Na^+ forms of Nafion and the styrene-based polyanions can be reliably titrated using DA^+ as the probe cation. Titrations involving the acid forms of these polyions were, however, unsuccessful; titration curves like that shown in Figure 6a were typically obtained. The rather drastic decrease in emission as the acid form of the polyanion is added to the DA^+ solution suggests that the quantum yield for DA^{++} is pH dependent. Figure 6b confirms this pH dependence in that a steady decrease in emission intensity for DA^{++} is observed when either HCl or HClO_4 is added to a DA^+ solution.

It is of interest to note that for equivalent amounts of H_3O^+ added, the decrease in emission produced by the polyacid is much greater than the decrease produced by the simple, monomeric acids (Figure 6). A possible explanation of this phenomenon is as follows:

It is well known that the local concentration of the counterion in the microenvironment around a polyelectrolyte chain can be much higher than the bulk solution concentration (16,17). When H_3O^+ is the counterion, this means that the local pH around the polyelectrolyte chain is much lower than the bulk solution pH. Therefore, DA^+ bound to chains containing some protonated $-\text{SO}_3^-$ sites will experience a local pH which is much lower than the bulk solution pH obtained upon addition of an equivalent amount of monomeric acid (HCl or HClO_4). Because of this lower microdomain pH, the emission intensity for the probe in the polyacid solution is attenuated more than the intensity for the probe in the monomeric acid solution.

Future studies will focus on the interesting pH effect shown in Figure 6. From the analytical point of view, however, the data in Figure 6 mean that the proton forms of the polyelectrolyte cannot be titrated using the procedure described here.

Determination of ϕ_c . According to equations 3 and 5,

$$I_{\text{max}}/I_0 = \phi_c/\phi_L \quad (8)$$

If I_0 and I_{max} can be obtained from the titration procedure described here, and if ϕ_L is known, ϕ_c can be easily calculated from equation 8. The quantum yield of the complex is of interest because it is an indicator of the nature of the probe-site interaction (18) and because it can be useful in a determination of the binding constant. To test the reliability of

equation 8, we compared ϕ_c for $\text{Ru}(\text{bpy})_3^{2+}$ - Nafion, obtained using the method of Parker and Rees (19) (alkaline fluorescein as reference), with ϕ_c calculated using equation 8. The data obtained are shown in Table II. The agreement between the two methods is excellent.

CONCLUSIONS

We have developed a new luminescence titration procedure for determination of either the EW of a polyanion or the concentration of the polyanion in solution. Extension of the method to titrations of polycations seems likely but would require a suitable anionic luminescence probe; we are currently searching for such a probe. The luminescence method is quick, easy and reliable. Acid-base titrations of polyelectrolytes can also be quick, easy and reliable. We have found, however, that sulfonated polymers are often contaminated with the monomeric acids used during the sulfonation procedure. Because of this, acid-base titrations frequently produce spuriously low EWs. The luminescence procedure described here is not affected by this contamination. For example, acid-base titration of our 1100 EW Nafion gave an EW of 1026 before dialysis and an EW of 1093 after dialysis. The luminescence procedure produced the same EW both before and after dialysis. Freedom from interference from monomeric acid is a major advantage of the luminescence procedure.

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Figure Captions

Figure 1. Effect of addition of various aliquots of a 0.1 (w/v)% solution of 100-NaPSS on the emission spectra of solutions of (a) DA^+ (4.0×10^{-5} M, volume = 2 mL); (1) = 0 μL , (2) = 6 μL , (3) = 9 μL , (4) = 12 μL , (5) = 15 μL , (6) = 18 μL , (7) = 28 μL added; (b) $\text{Ru}(\text{bpy})_3^{2+}$ (1.0×10^{-5} , volume = 1 mL); (1) = 0 μL , (2) = 1 μL , (3) = 3 μL , (4) = 3.8 μL , (5) = 8 μL , (6) = 10 μL .

Figure 2. Simulated titration curves (see text); (a) $K = 1000$, (b) $K = 100$, (c) $K = 10$. Vertical line marks theoretical equivalence point. Sloping and horizontal lines show extrapolations.

Figure 3. Titration curve using $\text{Ru}(\text{bpy})_3^{2+}$ as the lumophore. Vertical line marks theoretical equivalence point. $\text{Ru}(\text{bpy})_3^{2+}$ titrated with (a) Nafion, 0.474%, (b) NaPAS, 0.1%, (c) 100-NaPSS, 0.1%, (d) 6-NaPSS, 0.5%, (e) NaPMM, 0.2%.

Figure 4. Titration curves using DA^+ as the lumophore. Vertical line marks theoretical equivalence point. Horizontal and sloping lines show extrapolations. The polymers used and concentrations are the same as in figure 3.

Figure 5. Titration of 2.28×10^{-5} M DA^+ with 0.1% 100-NaPSS in the presence of 10^{-2} M NaCl. Compare curvature to figure 4c.

Figure 6. Effects of adding A. increments of a 0.315% 50-PSS (proton form) solution B. increments of a 1.0×10^{-2} M HClO_4 solution to 2 mL of 4.75×10^{-5} M DA^+ .

Table I. Accuracy and precision of the luminescence method.

Polymer	Nominal EW ^a	Measured EW		% Difference ^b
		Acid-Base	Luminescence	
Nafion	1100	1093 ± 23	1096 ± 18	0.3
100-PSS ^c	206	209 ± 1	208 ± 5	-0.5
50-PSS ^c	338	333 ± 3	334 ± 15	0.3

^aEW Specified by supplier.

^b% difference between luminescence and acid-base results.

^cH⁺ form used in acid-base titration; Na⁺ form used in luminescence titration; EWs expressed as Na⁺ form.

Table II. Quantum yields for $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+}$ - Nafion complex.^a

	Parker-Rees Method	Equation 8
$\text{Ru}(\text{bpy})_3^{2+}$	0.040 ^b	-
$\text{Ru}(\text{bpy})_3^{2+}$ - Nafion	0.075	0.077

^a $[\text{Ru}(\text{bpy})_3^{2+}] = 1 \times 10^{-6} \text{ M}$, Molarity of Nafion SO_3^- sites = $4 \times 10^{-6} \text{ M}$.
1200 E.W. Nafion.

^bLiterature value=0.042. K. Kalyanasundaram, Coord. Chem. Rev. 1982, 46, 159.

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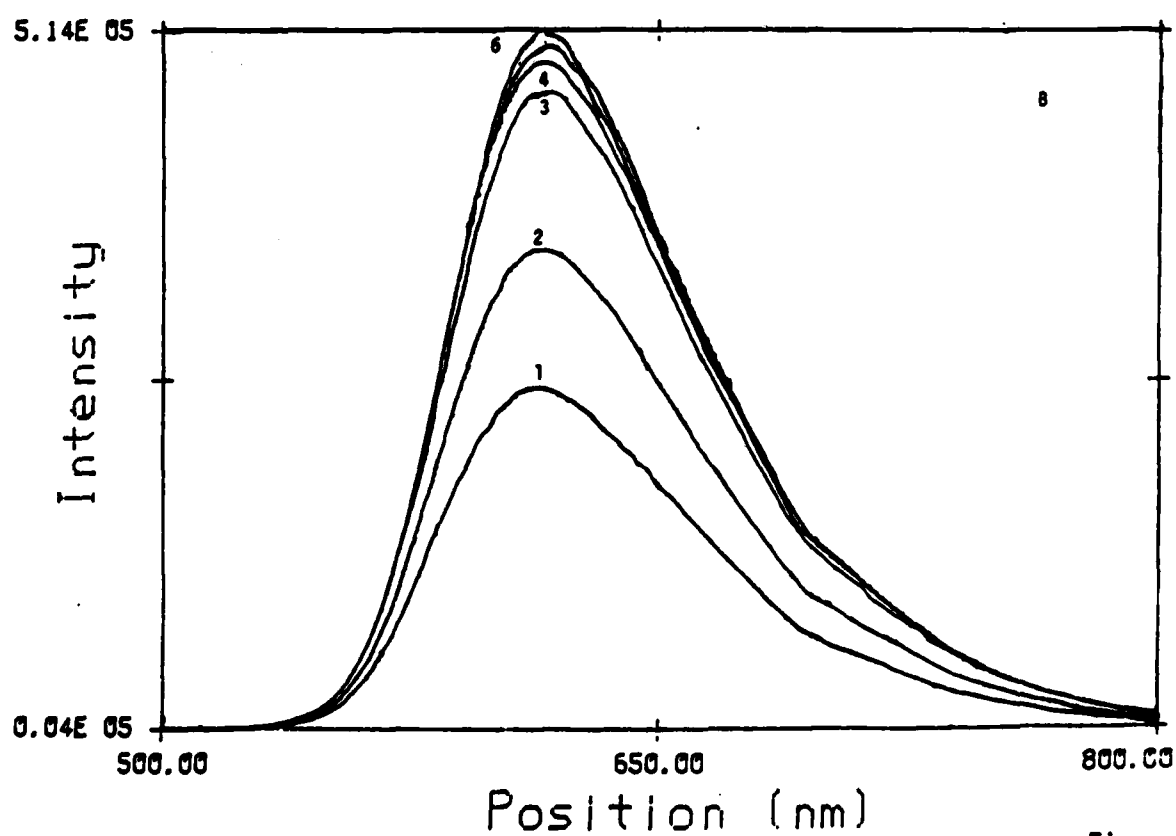
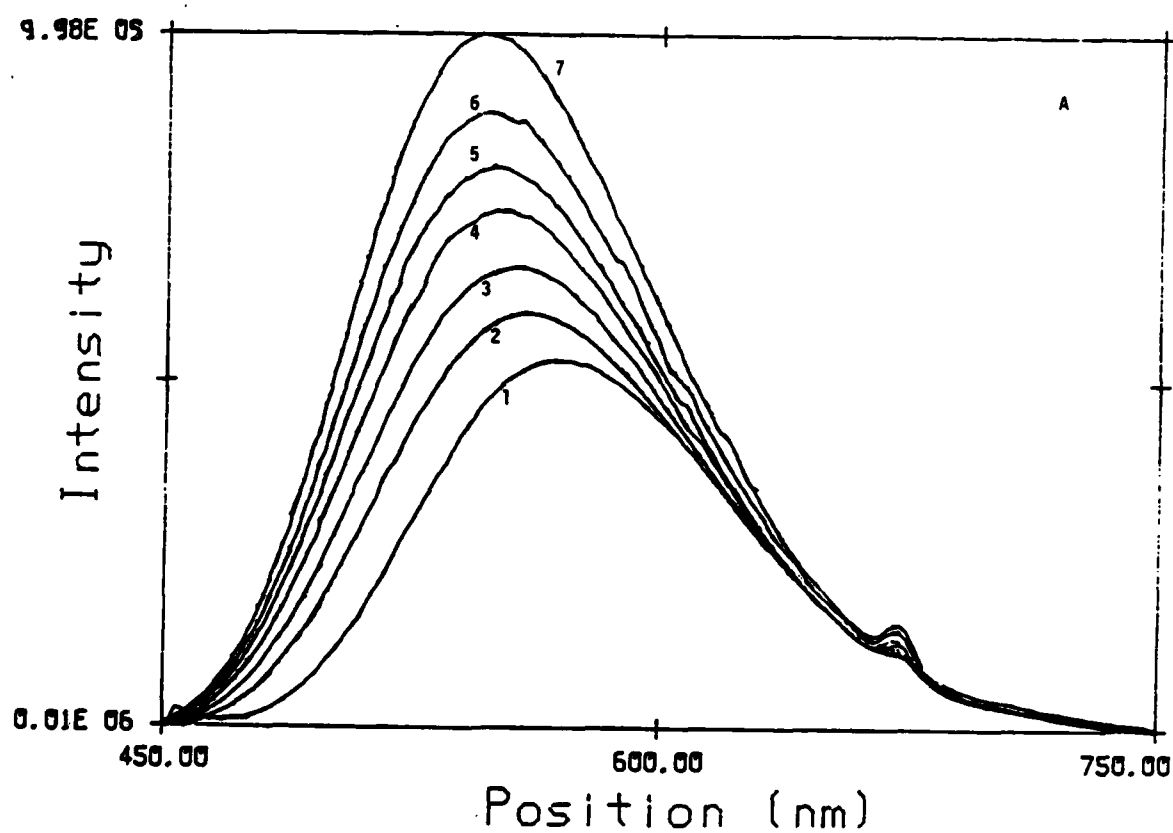


Figure 1

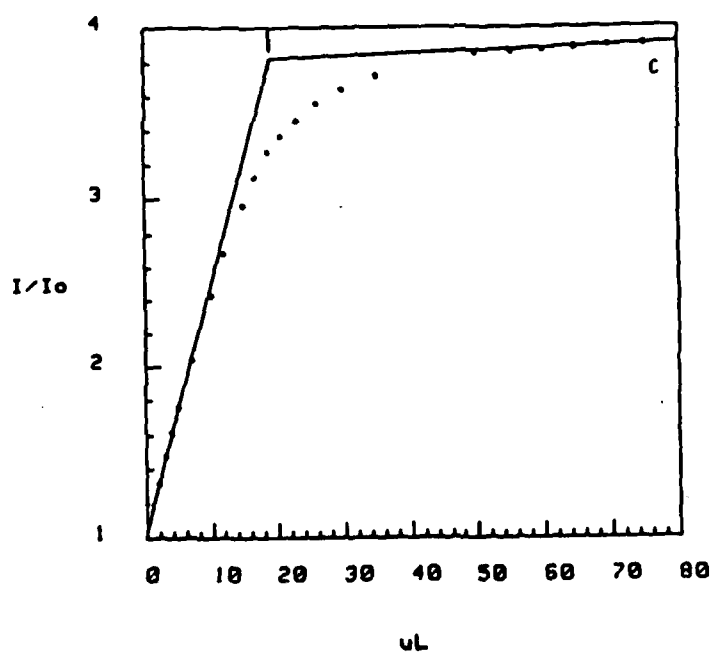
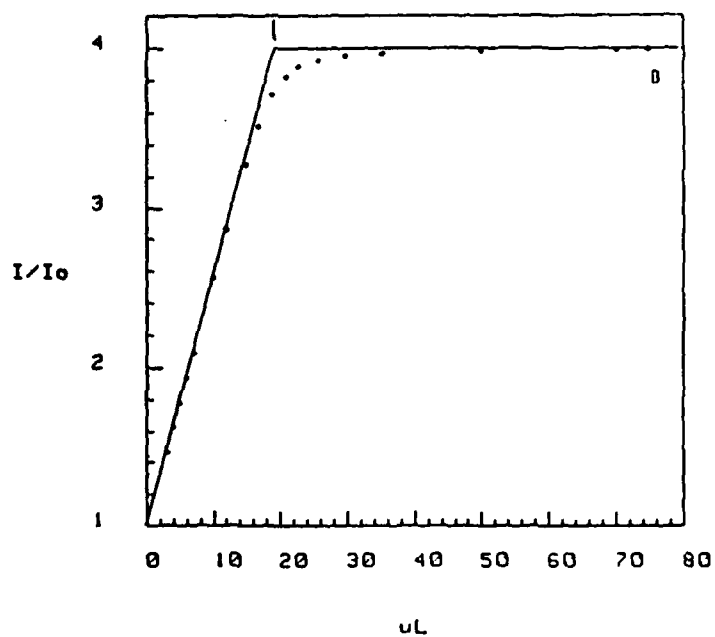
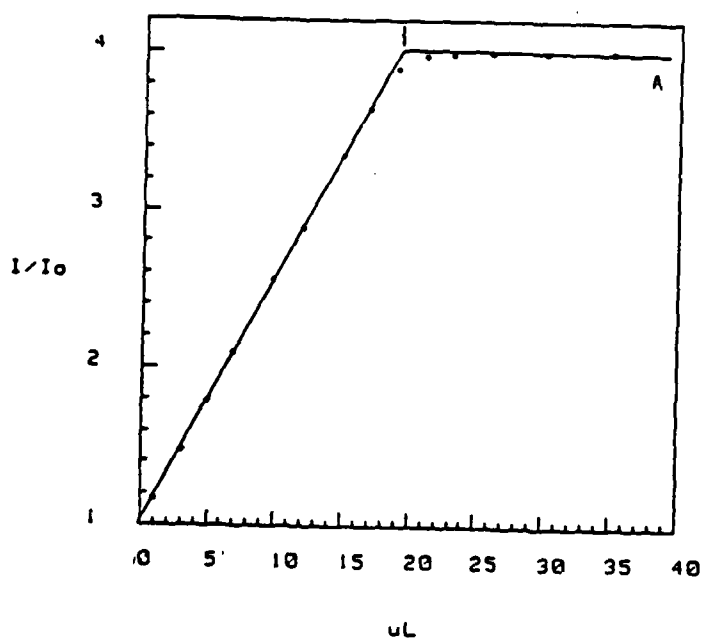


Figure 2

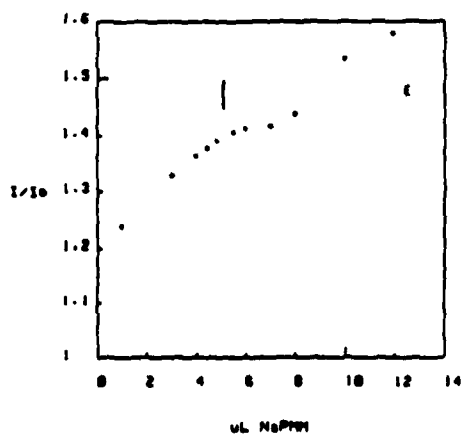
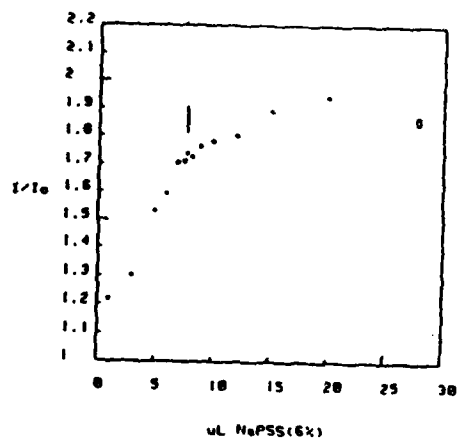
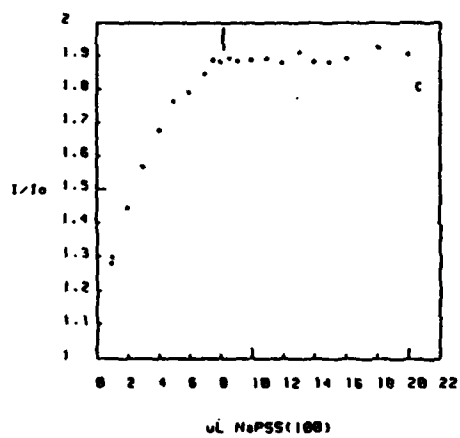
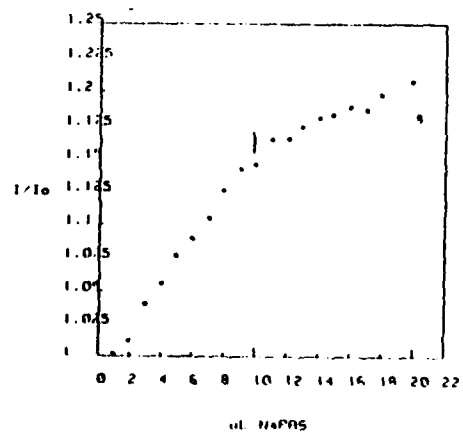
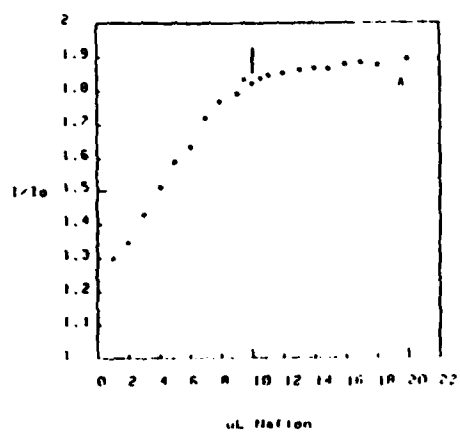


Figure 3

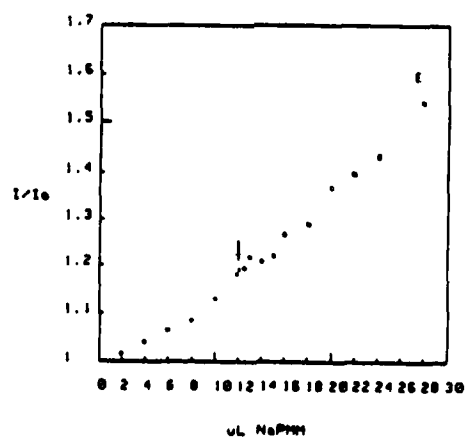
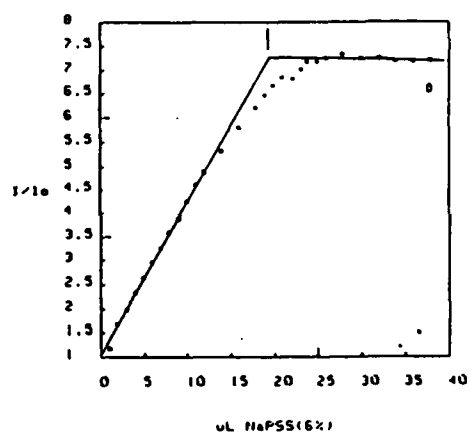
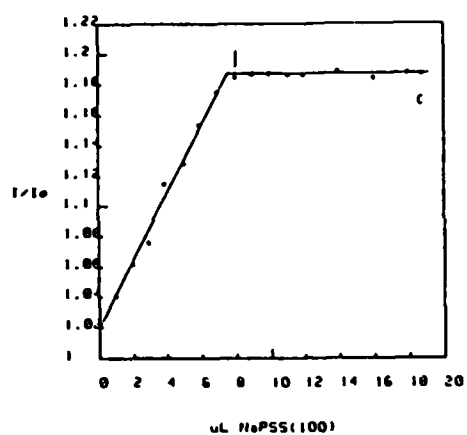
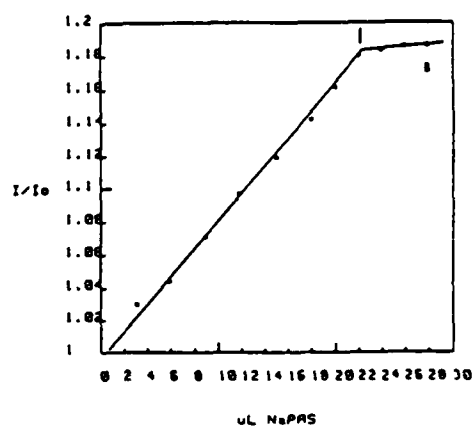
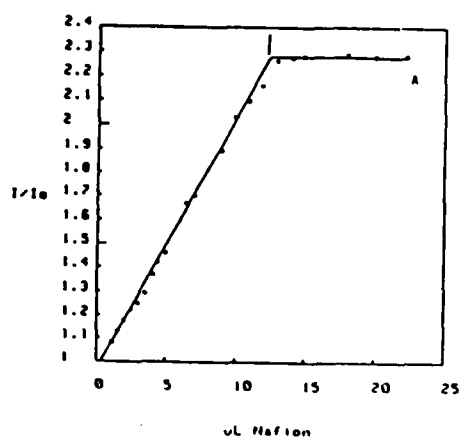
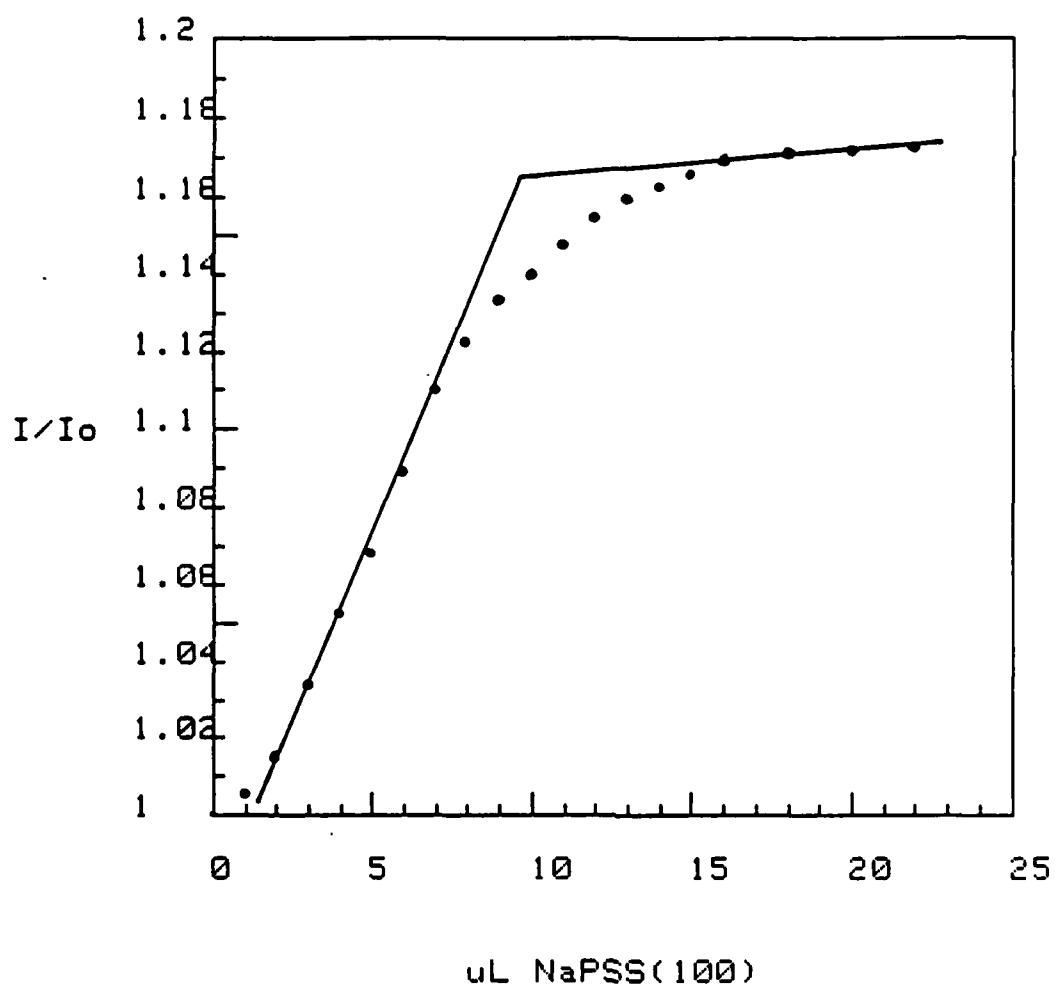
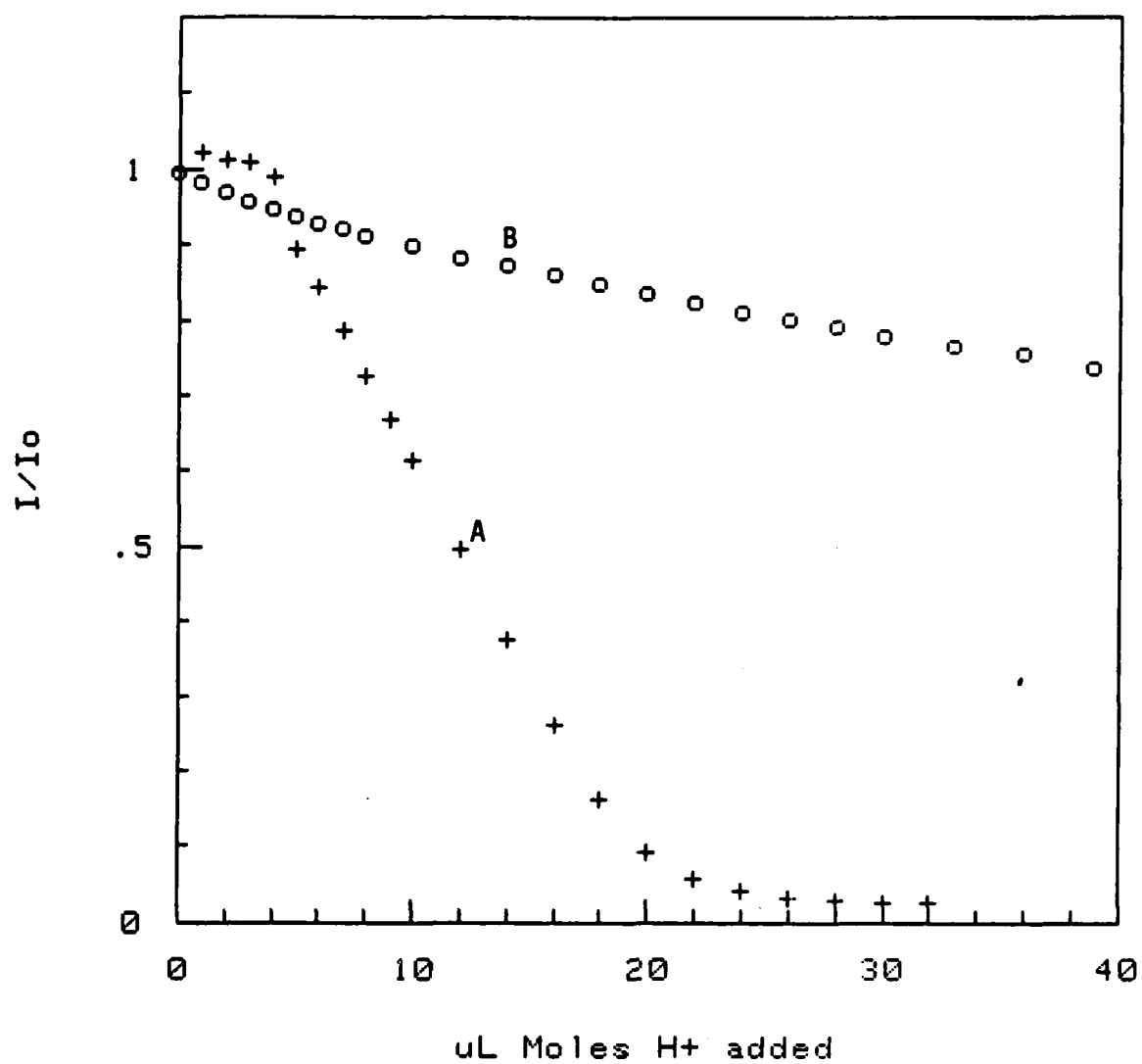


Figure 4





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